Available online at www.sciencedirect.com

ScienceDirect

Physics Procedia 8 (2010) 121–125

Physics Procedia

www.elsevier.com/locate/procedia

VI Encuentro Franco-Español de Química y Física del Estado Sólido
VI^{ème} Rencontre Franco-Espagnole sur la Chimie et la Physique de l'État Solide

Crystal growth of ZnO micro and nanostructures by PVT on c-sapphire and amorphous quartz substrates

D. N. Montenegro[1]*, S. Agouram[1], M. C. Martínez-Tomás[1], C. Llorens[1], C. Reig[2] and V. Muñoz-Sanjosé[1]

[1] *Dept. Física Aplicada i Electromagnetisme, Universitat de València, C/ Dr. Moliner 50, 46100 Burjassot, Spain*
[2] *Dept. Enginyeria Electrònica, Universitat de València, C/ Dr. Moliner 50, 46100 Burjassot, Spain*

Abstract

ZnO micro and nanostructures in the form of tripods, grains, arrows and wires have been grown at temperatures as low as 500-300 ºC by a vapour transport method without catalysis and using a well selected value of the carrier gas flow. A transition state between grains and nanowires is reported being characterized by arrow-like structures which are constituted by a pyramidal head and a tail that is growing from the basal plane of the head. In order to understand the effect of growth conditions on the morphology of micro and nanostructures, an analysis of temperature and species concentration conditions has been carried out. In addition two different kinds of substrates have been used, namely quartz and c-sapphire.

Keywords: ZnO microstructures, ZnO nanostructures, vapor phase, SEM.

1. Introduction

In recent years, ZnO nanostructures have attracted much attention due to their outstanding physical properties and wide variety of potential technological applications [1-3]. Different synthesis methods have been reported for ZnO nanostructures, but the vapor phase method (PVT) is probably the most extensively explored approach for the formation of different ZnO micro and nanostructures like multipods [4], tetrapods [5], tripods [6], nanorods [7], nanowires [8], etc. Some studies are reported on the effect of different growth parameters on the morphological pro-

* Corresponding author. Tel.: + 34963544617; fax: + 34963544908
E-mail address: diamon@alumni.uv.es

1875-3892
doi:10.1016/j.phpro.2010.10.022

perties of ZnO nanostructures grown by PVT. Recently K. Hou et al [9] reported the influence of deposition temperatures on morphologies of ZnO nanostructures in the temperature range 620-900 ºC. Also U. Manzoor et al. [10] investigated the growth of ZnO nanostructures between 750-900 ºC. In this range, nanorods, nanowires and nanocombs were synthesized. These studies are made at relative high temperatures and although there are important advances in the study of ZnO nanostructures, a better understanding of the correlation between growth conditions and morphologies is still necessary. Among other particularities low deposition temperature conditions favor the use of a wide family of substrates and reduce the diffusion effects between the substrate and the grown material. This low temperature conditions have been the focus of our work. The aim of this paper is to show that, after optimizing growth conditions, micro and nanostructures of ZnO can be obtained at temperatures as low as 300-500 ºC in a reproducible form. In this frame, a systematic study on the different obtained morphologies has been made. Additionally, it has been demonstrated that, under our experimental conditions, the growth of these nanostructures seems to be basically independent of the type of the used substrates, namely quartz and c-sapphire.

2. Experimental

ZnO micro and nanostructures were grown by a vapor transport method without catalyst. The experiments were carried out in a quartz tube placed in a two zones horizontal tube furnace. A mixture of ZnO with a 5N purity and graphite powder (10:1) was used as material source. It is known that the presence of graphite increases the yield of the evaporation process [11]. The mixed powder was kept into a ceramic boat and placed into a tubular furnace. The temperature of the source was maintained between 950-970 ºC for a time of 3h and cooled down at room temperature during a time of 5 h. The temperature of the deposition zones ranged between 300-500 ºC. Polished amorphous quartz and c-sapphire were used as substrates as received and were placed at different distances from the material source. One end of tube furnace was connected to a flow-meter system and the other end to an evacuation hose. Ar flow (100 sccm) was introduced as carrier gas during the growth process and maintained until the system was cooled to room temperature. The hose was used in order to facilitate the evacuation of the residual material and to isolate the growth process from external contaminations. Surface morphologies of ZnO micro and nanostructures were examined by scanning electron microscopy (SEM-Hitachi S4100) and its crystalline structure by X-ray diffractometry (XRD) in the facilities of the *Servei Central de Suport a la Investigació Experimental (SCSIE)* at the University of Valencia (Spain).

3. Results

Figure 1 shows the SEM images of ZnO structures grown on amorphous quartz substrates at several deposition temperature ranges. As a general trend, it can be said that grains appear in all ranges, but with different sizes and morphologies (Figure 1). At the higher temperature edge of the first range (470-420), tripods are found, having their

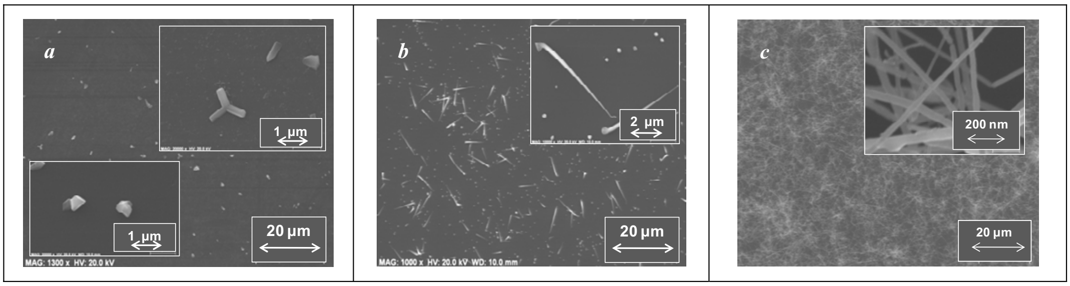

Figure 1. Typical SEM images of ZnO nanostructures grown at several deposition temperatures on quartz substrates: (a) 470-420 ºC, (b) 420-370 ºC, (c) 350-300 ºC. The insets correspond to magnified representative images of each deposited region.

legs a length of about 600-800 nm and a width of about 300-500 nm. The grains in this range have the form of hexagonal prisms and pyramids with a mean width of about 500 nm (Figure 1a). In the mean temperature range (420-370 ºC), grains and structures like arrows appear (Figure 1b). We have not found other reports on these ZnO arrow-like structures in the literature. The SEM image with higher magnification of the inset shows that arrows are constituted by a pyramidal grain with a tail in its basal plane. The total length of arrows is about 3-6 μm, having the heads and the tails a diameter of about 500 nm.

At the lowest deposition temperature range, 370-300 ºC, very small grains and nanowires are synthesized. These nanowires form a cloud and look as grown from the small grains. The average diameter of nanowires decreases when the deposition temperature decreases. In the high edge of this lower temperature range the diameters are between 400-200 nm (image not shown) while in the lower temperature edge the diameters are significantly smaller (200-50 nm) (Figure 1c).

On c-sapphire substrates (Figure 2) similar structures to those on quartz are obtained. In the temperature range of 500-430 ºC (Figure 2a) tripods are not found and only grains are present, having the form of hexagonal prisms and pyramids. In the mean range 430-385 ºC (Figure 2b) arrows are also obtained, having the head a more defined pyramidal form. Nanowires are also present in the lower temperature range 385-320 ºC (Figure 2c). Nanowires are grown from the base of small grains. It can be seen that the sizes of ZnO structures are basically of the same order on both types of substrates.

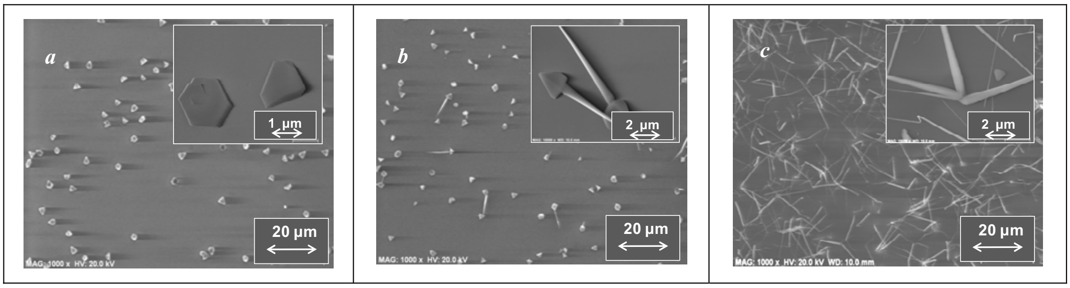

Figure 2. Typical SEM images of ZnO nanostructures grown at several deposition temperatures on c-sapphire substrates: (a) 500-430 ºC, (b) 430-385 ºC, (c) 385-320 ºC.

As a differential behavior in respect of quartz, ZnO grains are better defined (up inset of Figures 2a and 2b). However, the obtained structures are morphologically similar. The deposition on sapphire at the higher temperature range can look like a film but a comparison between not tilted/tilted images of SEM cross sectional views (Figures 3a and 3b) reveal the isolated grain morphology.

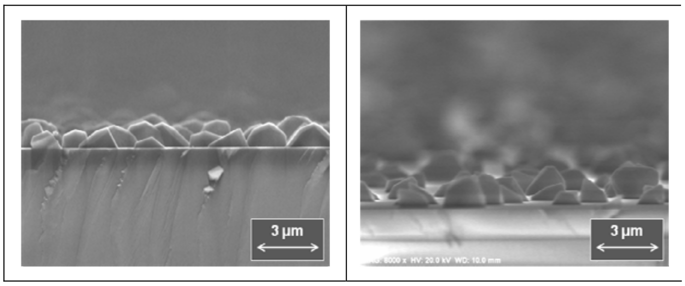

Figure 3. (a) Non-tilted and (b) tilted SEM cross sectional views of ZnO grains on c-sapphire substrates at the temperature range of 500-430 ºC.

Figure 4 shows a representative XRD pattern of ZnO samples grown on amorphous quartz and c-sapphire substrates. The diffraction peaks can be indexed to the hexagonal structure of ZnO with lattice constants of a=0.324982 nm and c=0.520661 nm. It is observed that on samples grown on quartz, the ZnO peaks are hardly distinguished from the background while on sapphire are clearly marked. This characteristic is compatible with the existence of more defined grains in the case of sapphire. If the facets of the grains are flatter and more oriented they will give rise to a more efficient diffraction in comparison with a less defined or lower ordered grain structure.

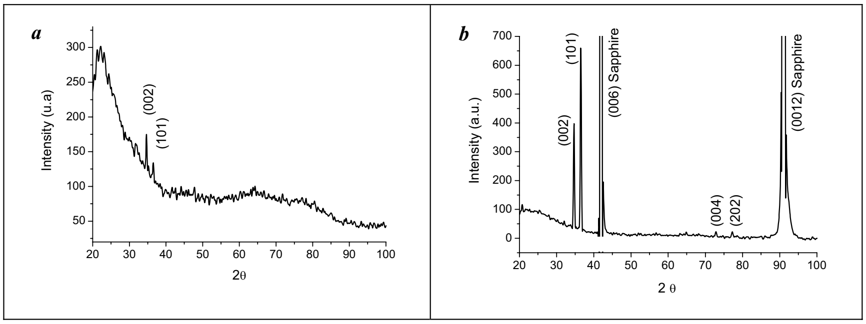

Figure 4. Representative XRD patterns of ZnO nanostructures samples on different substrates, (a) amorphous quartz, (b) c-sapphire.

4. Discussion

The most accepted growth models for the growth of ZnO nanowires are the vapor-liquid-solid (VLS) and the vapor-solid (VS). For the VLS model, the driving force for the growth is the precipitation and nucleation at the liquid-solid interface, where the size of the growing structure depends both on the composition and size of the liquid droplet. For the VS model, the structure growth is mainly controlled by kinetics, for which the temperature and the supersaturation ratio are two dominant processing factors regarding the morphology of the products. In our case, since no droplets have been observed at the end of the analyzed nanowires and the temperature range, we can admit that the VS is the dominant mechanism. Related to the growth habit of ZnO, it is known that the (0001) faces are the highest-energy low-index planes, thus being thermodynamically favored and, consequently, they produce a fast growth along the [0001] direction [12].

In our case, we have found structures ranging from grains, then arrows, and finally wires when temperature ranges from high to low temperatures. The structures are better defined on sapphire substrates than on quartz substrates. These results can be analyzed by considering the joint effect of nucleation and growth conditions.

Related to the size, once the carrier gas flow has been optimized, temperature seems to be the main factor. Moreover, each deposition temperature corresponds to a different position and, then, to a different distance from the sublimation source and to a different supersaturation condition, depending on the concentration gradient. Thus, both factors make that samples near the source have more favorable growth conditions and a higher growth rate, reaching the structures bigger sizes. This behavior is mainly observed on grains and it is confirmed by the fact that also the width of the wires decrease as the temperature decreases.

In respect of morphology, the relatively high temperature leads to growth conditions near the source making the grains to grow as expected, regarding the different growth rate of the different crystallographic planes. We observe that the seeds are pyramids or hexagonal columns. However, as we move from the source, the poorer growth conditions (temperature and supersaturation) generate smaller and isolated grains. These conditions also produce some thermal or strain instability at the solid-vapor interface giving rise to singular nucleation points that enhance a one-dimensional growth at this point. As in the lower temperature zone nanowires are observed while in the mid temperature zone arrows are seen, we can consider these structures as characteristics of a transition zone between grains and nanowires. At lower temperatures, the very poor growth conditions make the grains to be very small and the growth of the tail is enhanced in respect of that of the grain, resulting on the typical one dimensional growth of nanowires. We have obtained explicit arrows in a repetitive form in the range of 410-370 ºC. Until our knowledge this transition zone has not been so clearly shown before.

ZnO tripods are observed on quartz substrates close to the source. They look like having an isolated core from which three branches are developed. It seems that good growth conditions (temperature and supersaturation) enhance the presence of additional nucleation points on the grains. Legged nanostructures are in the scope of some optoelectronic devices. In fact, recently ZnO nanotetrapods have been used as multiterminal sensors to detect light with different wavelengths, being sensitive to ultraviolet light and exhibiting advantages for distinguishing noise [13]. ZnO tripods are less studied and controversial growth mechanisms have been proposed [6,14]. Both technological applications and academic interest will make these nano-microstructures the object of further studies now in progress.

5. Conclusions

In summary, ZnO micro and nanostructures in the form of tripods, grains, arrows and wires have been obtained at temperatures as low as 500-300 ºC by a vapor transport method without catalysis by using a well selected value of the carrier gas flow. An analysis of the growth conditions indicate that both temperature and concentration conditions are key points to obtain grains of different sizes and different structures related with them. Both factors affect the morphology of the grains, favoring nucleation points on its basal plane and producing arrows and nanowires. Arrows seem to be and intermediate state between grains and wires. The study of growth on different substrates indicates that under our experimental conditions the growth of nanostructures is free enough to not be significatively affected by the type of substrate.

References

[1] Z.L.Wang, Materials Science and Engineering R 64 (2009) 33–71.

[2] C. Klingshirn, phys. stat. sol. (b) 244, 9 (2007) 3027– 3073.

[3] L. Schmidt-Mende and J. L. MacManus-Driscoll Materialstoday 10 (2007) 40-48.

[4] Y.H. Leung, A.B. Djurisic, W.C. H. Choy, M.H. Xie, J. Gao, K.W. Cheah, K.Y. K. Mand, W.K. Chand, Journal of Crystal Growth 274 (2005) 430–437.

[5] K. Zheng, C. X. Xu, G.P. Zhu, X. Li, J.P. Liu, Y. Yang, X.W. Sun Physica E 40 (2008) 2677-2681.

[6] S. Mandal, A. Dhar and S.K. Ray Appl. Phys. 105 (2009) 033513.

[7] M. Biswas, E. McGlynm, M.O Henry Microelectronics 40 (2009) 259-261.

[8] H.W. Kim, M.A. Kebede, H.S. Kim, B. Srinivasa, D.Y. Kim, J.Y. Park, S.S. Kim Current Appl. Phys. 10 (2010) 52–56.

[9] K. Hou , C. Li, W. Lei, X. Zhang, X. Yang, K. Qu, B. Wang, Z. Zhao, X.W. Sun Physica E 41 (2009) 470-473.

[10] U. Manzoor, D. Kyung Kim Physica E 41 (2009) 500-505.

[11] R. Tena-Zaera, C. Martínez-Tomás, C. J. Gómez- García, and V. Muñoz-Sanjosé Cryst. Res. Technol. 41 (2006) 742-747.

[12] Z.L.Wang, J. Phys.: Condens. Matter 16 (2004) R829–R858

[13] J. Li, H. Peng, J. Liu and H. O. Everitt Eur. J. Inorg. Chem. 2008 (2008) 3172-3176.

[14] M.Y. Choi, H.K. Park, M.J. Jin, D.H. Yoon, S.W. Kim Journal of Crystal Growth 311 (2009) 504-507.